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Catalytic oligomerization of α-olefins in the presence of two-stage activated zirconocene catalyst based on 6,6-dimethylfulvene 'dimer'

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S1. General experimental remarks

All synthetic manipulations were performed under argon atmosphere. Toluene, diethyl ether, and THF were refluxed with Na/benzophenone/dibenzo-18-crown-6, and distilled prior to use. Pentane and hexanes were refluxed over Na/K alloy for 12 h, and then distilled. CH_2Cl_2 was washed with aqueous Na_2CO_3, stirred with $CaCl_2$ powder, refluxed over CaH_2 for 8 h, and distilled. $CDCl_3$ was distilled over P_2O_5 and stored over 4 Å molecular sieves. Metallocene synthesis was performed by using standard Schlenk technique. Butyllithium (1.6 M solution in hexanes) was used as purchased (Aldrich).

NMR spectra were recorded on an Avance Bruker spectrometer (400 MHz) in $CDCl_3$ using CH_2Cl_2 (δ = 5.30) as an internal standard, and in THF-d_8. Chromatography analysis was performed using a Kristall-2000M chromatograph (GC) or an Agilent PL-GPC-220 gel permission chromatograph (GPC).

S2. Preparation of 4

3-(1,3-Cyclopentadien-1-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydropentalene **5** (mixture of isomers). Solution of $NaN(SiMe_3)_2$ (3.1 g, 20 mmol) in THF (20 ml) was added to a cooled (0 °C) solution of 6,6-dimethylfulvene (21.2 g, 200 mmol) in THF (180 ml). The mixture was allowed to warm to room temperature, stirred for 8 h, poured into 200 ml of 5% aq. NH_4Cl, extracted with pentane (3×100 ml). The combined organic fractions were dried over $MgSO_4$, evaporated under reduced pressure and distilled *in vacuo* collecting the fraction with bp 95-105 °C / 0.05 Torr. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.10-1.44 (group of s, 9H); 2.15 (m), 2.43 (m) {2H}; 2.79 (bs, 2H); 2.95 (bs, 2H); 5.78-6.49 (group of m, 5H). The yield was 13.2 g (62%, pale yellow liquid).

The crude product (13.2 g, 62 mmol) was dissolved in ether (200 ml), the solution was cooled to -20 °C, and n-BuLi (100 ml, 1.6 M in hexanes, 160 mmol) was added. After slow

heating to room temperature and 2 h of stirring, the colorless precipitate of dilithium derivative **5a** was filtered off and dried *in vacuo*. The yield was 8.9 g (64%). ^{1}H NMR (THF-d_8, 20 °C): δ 1.21 (s, 3H); 1.29 (s, 3H); 1.74 (s, 3H); 2.16 (d, 1H, ^3J = 12.5 Hz); 2.86 (d, 1H, ^3J = 12.5 Hz); 5.10 (m, 1H); 5.21 (m, 1H); 5.47 (m, 1H); 5.68 (m, 2H); 5.68 (m, 2H). The product contains Et_2O (1:1).

η^5-3-(η^5-Cyclopentadienyl)-1,1,3-trimethyl-1,2,3,4-tetrahydropentalenyl dichloro-zirconium (IV) **4**. Suspension of **5a** (3.51 g, 11.8 mmol) in ether (50 ml) was cooled to -40 °C, and Me_3SnCl (5 g, 25 mmol) in ether (20 ml) was added with stirring. The mixture was allowed to warm to room temperature, and filtered. The filtrate was evaporated under reduced pressure, toluene (20 ml) was added and then evaporated for complete elimination of ether. The residue was dissolved in toluene (40 ml), $ZrCl_4$ (2.8 g, 12 mmol) was added with stirring. After 6 h at 60 °C the mixture was cooled to room temperature, the solution was separated by decantation, and evaporated to c.a. 15 m. Hexane (10 ml) was added. After 16 h of crystallization at 0 °C, the product was filtered off, washed with pentane and dried *in vacuo*. The yield was 2.72 g (62%), yellowish crystals. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.31 (s, 3H); 1.38 (s, 3H); 1.92 (s, 3H); 2.48 (1H); 2.87 (1H) {AB, ^2J=14.4 Hz, -CH_2-}; 5.46 (d 1H); 5.82 (m, 2H); 6.24 (m, 1H); 6.51 (q, 1H); 6.70 (t, 1H); 6.78 (q, 1H). ^{13}C NMR ($CDCl_3$, 20 °C): δ 24.9; 26.6; 38.5 {-CH_3 }; 40.2; 46.2 (>C<); 55.4 (-CH_2-); 100.2; 106.4; 109.7; 114.5; 116.5; 125.6; 127.4 {-CH=}; 121.5; 125.2; 144.0 {>C=}. For $C_{16}H_{18}Cl_2Zr$, 372.44 Calc.: C 51.60% H 4.87; Found: C 51.22% H 4.90%.

S3. Oligomerization experiments

Alk-1-ene (200 mmol) and a 1 M TIBA solution in hexane (2 ml, 20 mmol) were mixed in a two-necked flask prefilled with argon, which was then placed in a thermostated bath with diethylene glycol. After maintaining the external bath at 60 °C for 5 min, the corresponding zirconocene dichloride (0.1 mmol) was added to the flask. After 20 min of stirring, a 1.5 M MAO solution (0.66 ml, 1 mmol) was added to the mixture. After 4 h of stirring, the mixture was cooled to room temperature, 1 ml of water and 1 ml of MeOH were added. The mixture was filtered through 5 mm neutral aluminia, and evaporated under reduced pressure yielding a mixture of oligomers (complexes **1, 3, 4**) or viscous polymeric product (complex **2**).

S4. ^{1}H NMR monitoring

Figure A1 shows the NMR spectrum of the initial reaction mixture for hex-1-ene oligomerization in the presence of zirconocene catalysts after addition of MAO (no appreciable conversion). In order to obtain reference spectra, the hex-1-ene dimer, trimer, and tetramer were isolated in a pure state. Their ^{1}H NMR spectra are shown in Figs. S2-S4. Also, Fig. S5 shows the spectrum of a mixture of hex-2-enes formed as by-products in the dimerization.

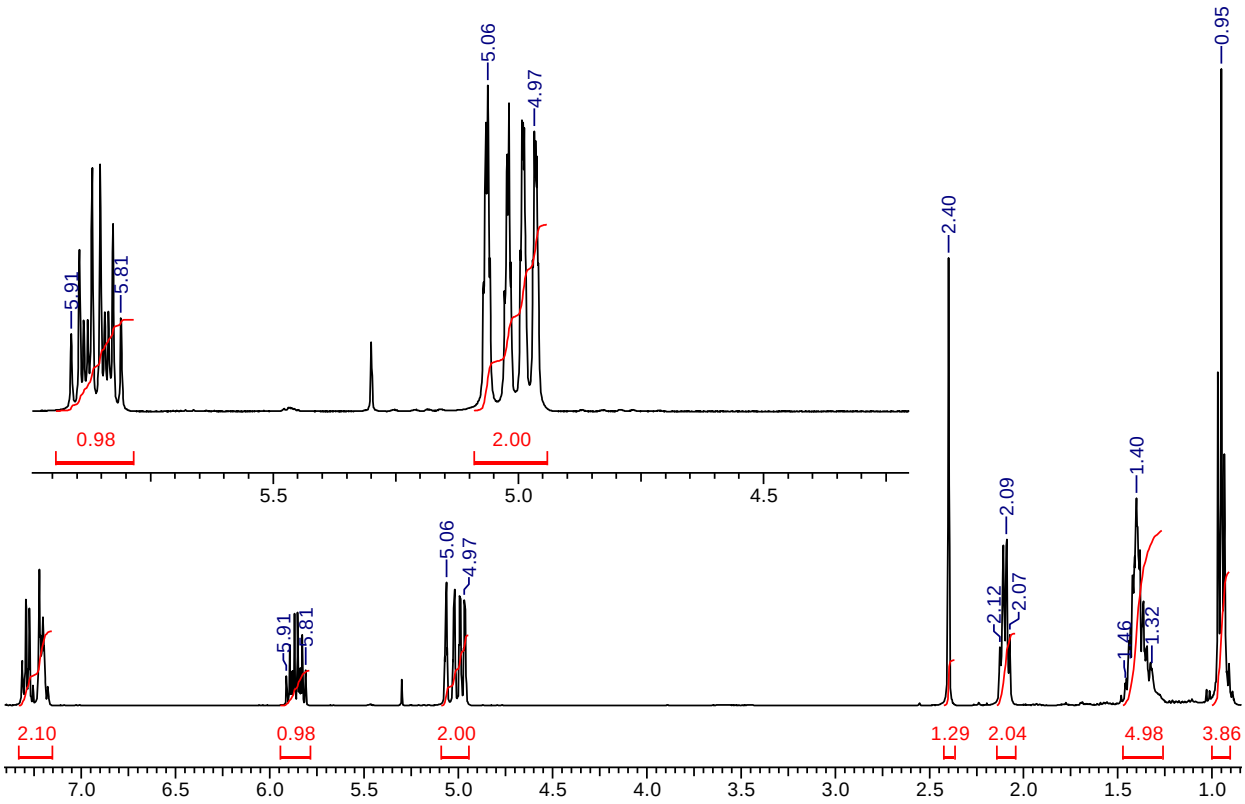

Figure S1 ^{1}H NMR spectra of the initial reaction mixture. The mixture contains hex-1-ene (200 mmol), TIBA (2 mmol), MAO (1 mmol, 0.65 ml of 1.5 M toluene solution), Cp_2ZrCl_2 (**1**, 0.1 mmol), and toluene (6 ml).

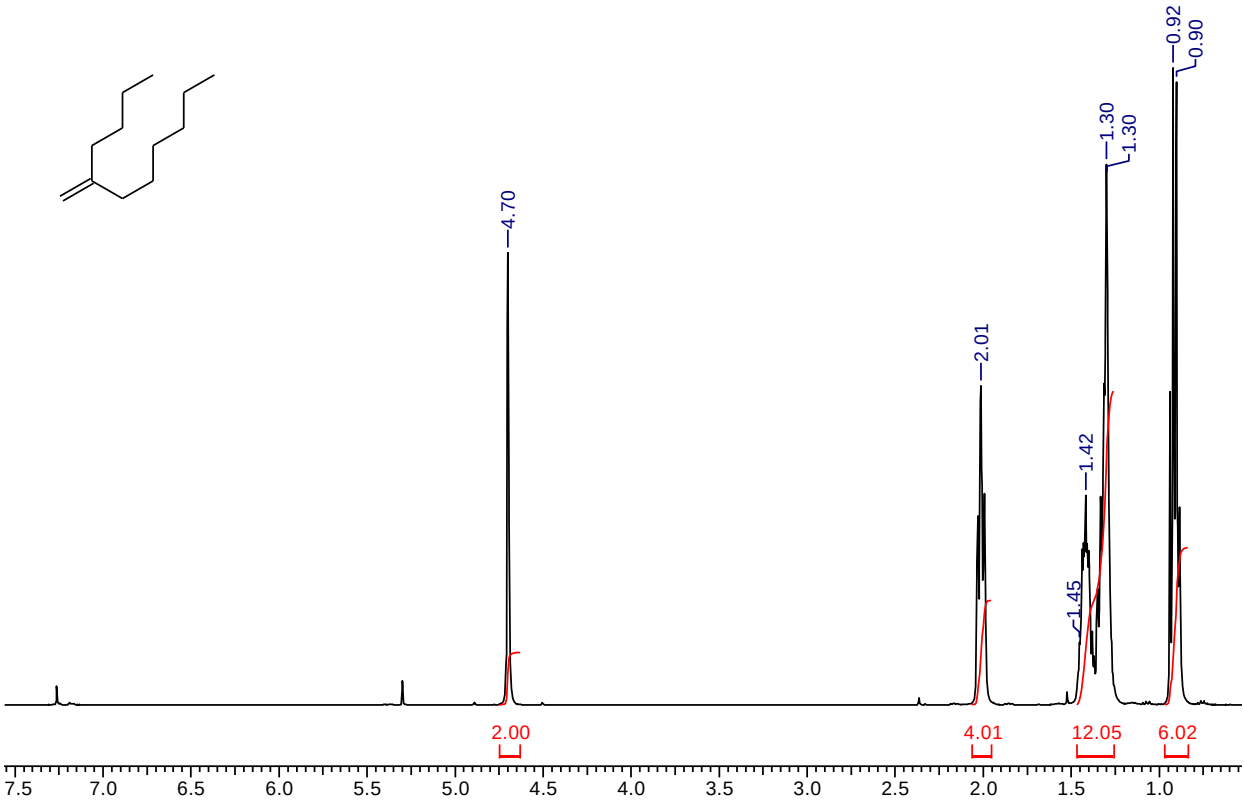

Figure S2 ^{1}H NMR spectra of 2-butyloct-1-ene (dimer of hex-1-ene).

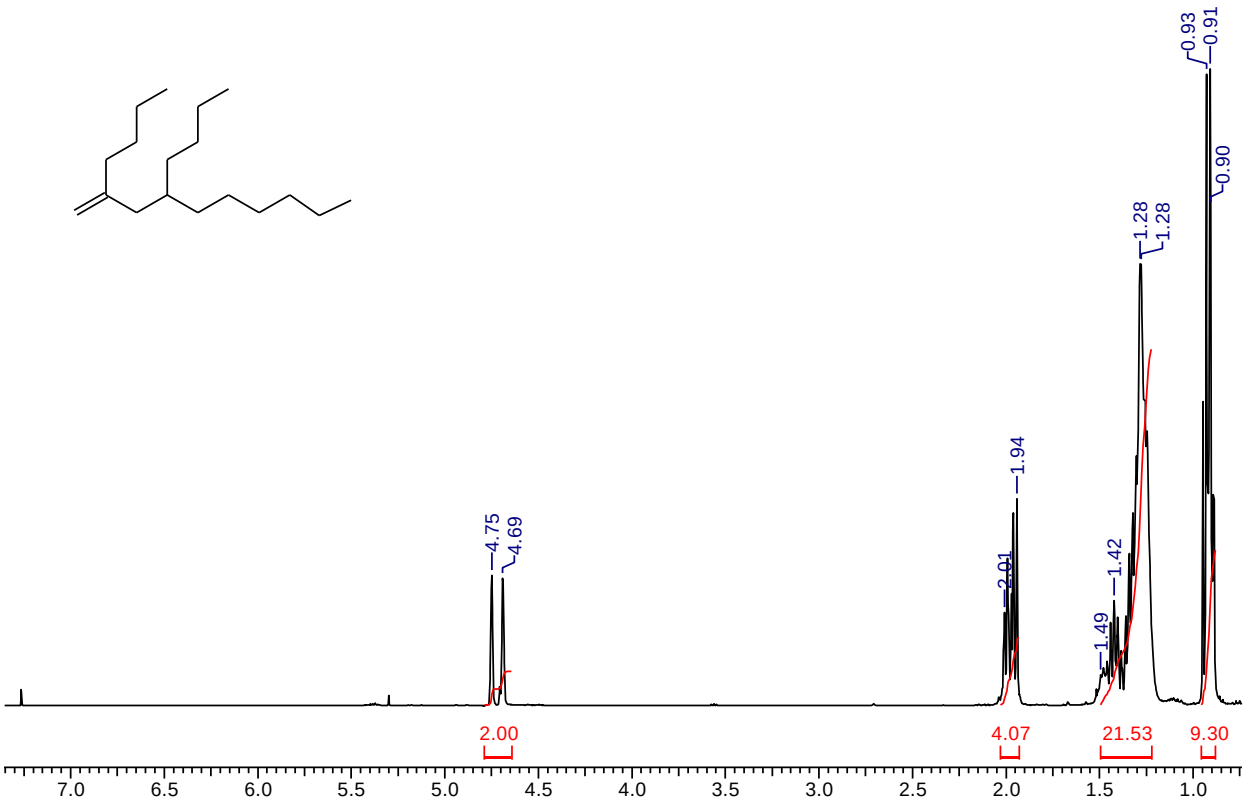

Figure S3 ^{1}H NMR spectra of 2,4-dibutyldec-1-ene (trimer of hex-1-ene).

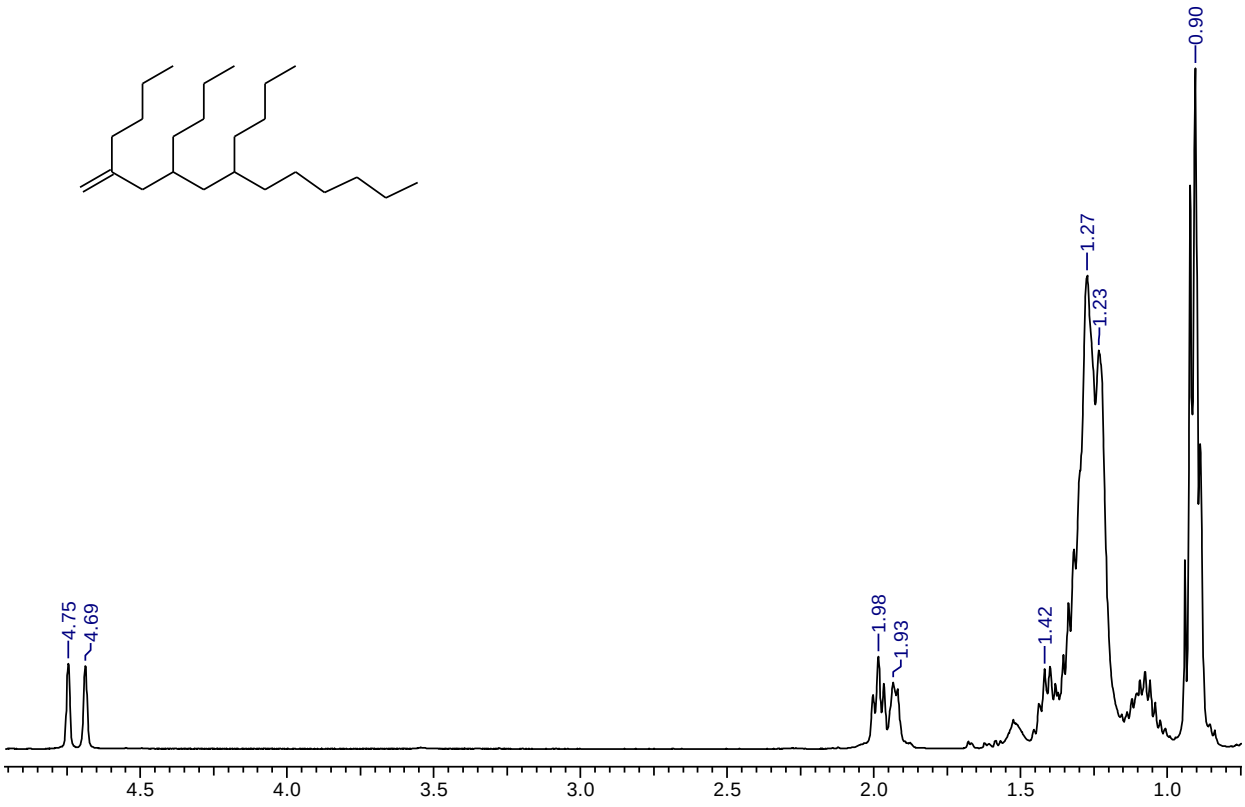

Figure S4 ^{1}H NMR spectra of 2,4,6-tributyldodec-1-ene (tetramer of hex-1-ene).

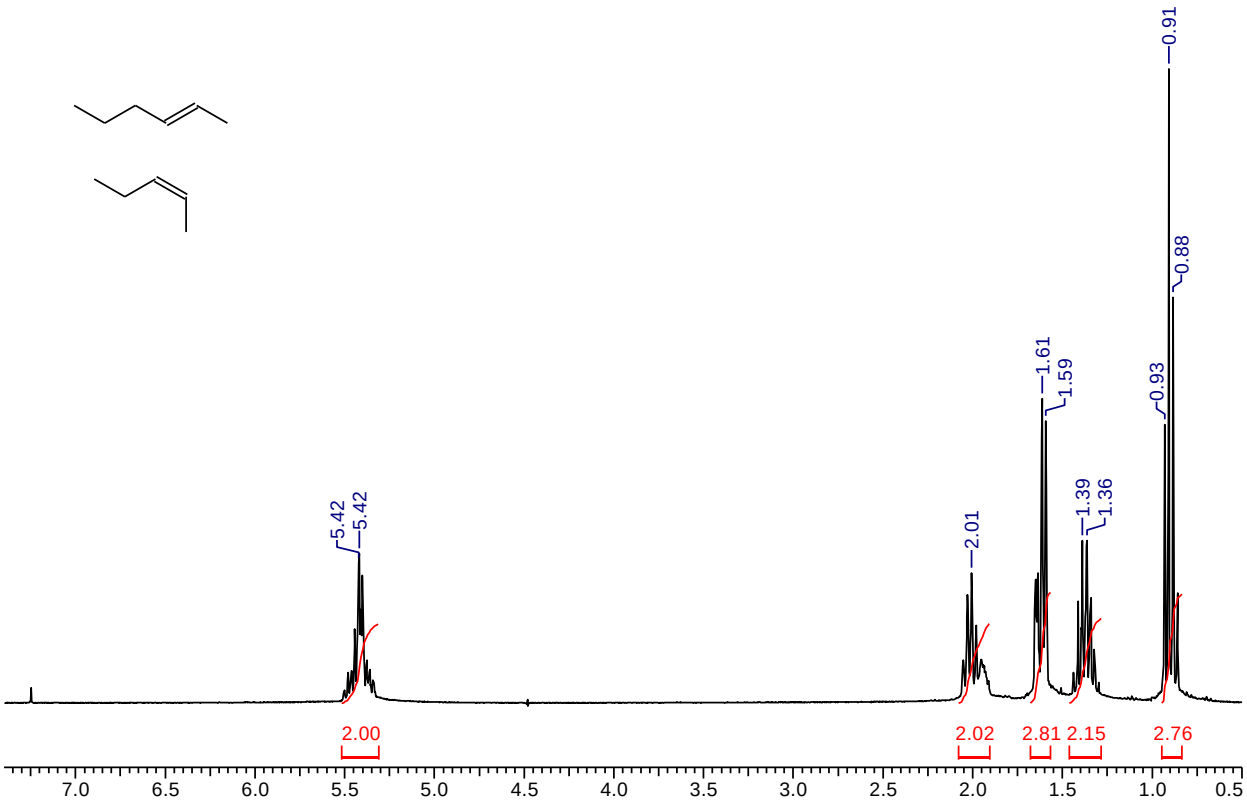

Figure S5 ^{1}H NMR spectra of (*Z*)- and (*E*)-isomers of hex-2-ene.

When hex-1-ene dimer is formed as the major reaction product, the composition of the reaction mixture can be determined fairly accurately by analyzing the relative signal intensities in the region of δ = 4.2-6.0 ppm. The calculation is performed after determination of the integrated intensities for the following signals:

- INT in the region of 5.4-5.5 ppm corresponding to hex-2-ene isomers (2H for C_6 molecule);
- SUB in the region of 4.92-5.04 ppm corresponding to hex-1-ene (2H for C_6 molecule);
- TRI at 4.75 ppm corresponding to hex-1-ene trimer (and tetramer the content of which is very low and introduces a minor error of calculations) 1H for C_{18} molecule;
- DI at 4.97-4.73, a signal of hexene dimer (2H for C_{12} molecule) plus the second $=CH_2$ component of the hexene trimer (1H for C_{18} molecule). Thus, the integrated intensity of the signals of hexene dimer is DI-TRI.

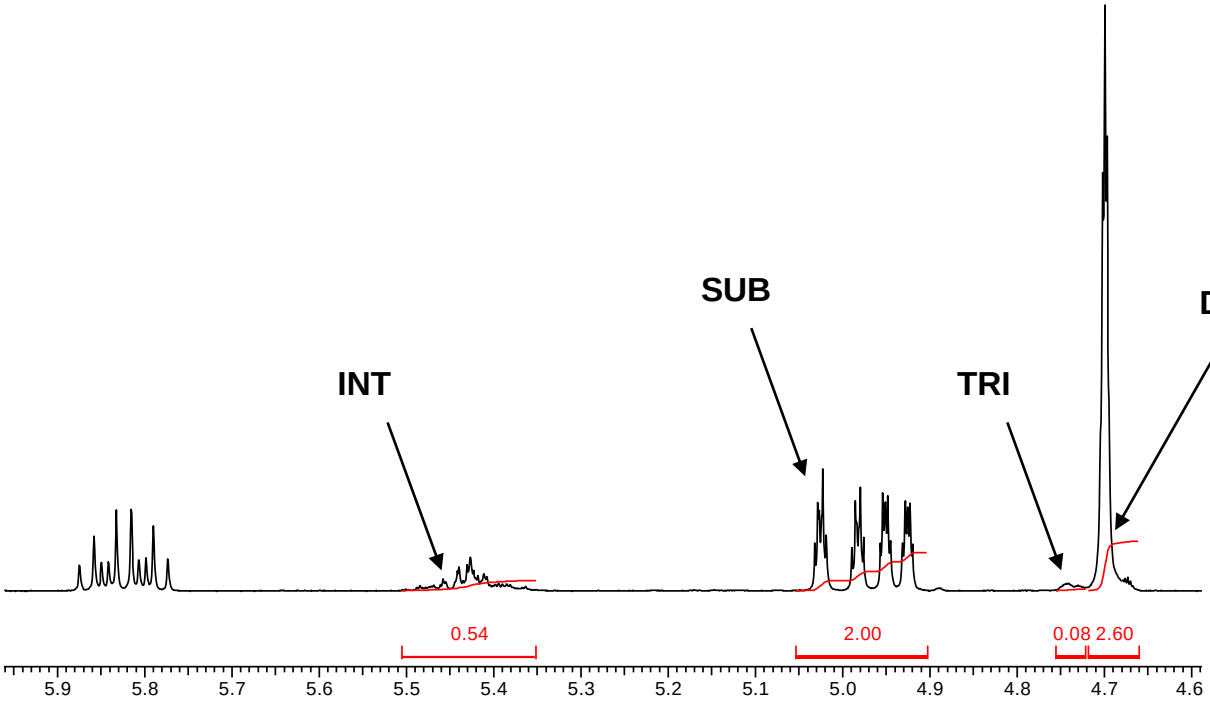

Figure S6 Signals used to calculate the composition of reaction mixture of hexene dimerization in the presence of **1** on the basis of the ^{1}H NMR spectrum.

These integrated intensities can be used to calculate the percentage of the substrate, isomerization products (hex-2-enes), dimers, and higher hexene oligomers. This calculation is well-posed in the context of our task: the search for effective dimerization catalysts providing low level of formation of hexene tetramer and higher oligomers.

Considering the mass balance of the reaction, the weight fractions of the components can be calculated from the integrated intensities of the INT, TRI, and DI signals obtained for SUB = 2 according to the following relations:

$$\% \text{ dimer in the mixture} = (DI–TRI)/(1+TRI\times3+(DI–TRI)+0.5\times INT)\times100$$

$$\% \text{ oligomers in the mixture} = TRI\times3/(1+TRI\times3+(DI–TRI)+0.5\times INT)\times100$$

$$\% \text{ 2-hexenes} = 0.5\times INT/(1+TRI\times3+(DI–TRI)+0.5\times INT)\times100$$

$$\% \text{ initial 1-hexene} =1/(1+TRI\times3+(DI–TRI)+0.5\times INT)\times100.$$

For the spectrum shown in Fig. S6 (INT =0.49; SUB =2; TRI = 0.06; DI = 0.63), using these relations gives 62.5% dimer, 6% trimer and oligomers, 6.1% 2-hexene, and 25% unreacted 1-hexene.

When higher oligomers of hex-1-ene are formed as the major reaction products, it is improper to estimate the composition of the mixture from the integrated intensities of the olefinic proton signals. In view of the fact that the experiments were carried out under standard conditions, actually, in the presence of an internal standard not involved in the reaction (toluene, 2.1 integrated intensity in the beginning of the reaction, Fig. S1) and with known amounts of hexane (a TIBA solution, contribution to the integrated intensity of the $–CH_2–$ and >CH–

aliphatic proton signals equal to 1, Fig. S1), the quantitative composition of the mixture can be roughly estimated from analysis of the integrated intensities of the following signals (Fig. S7):

SUB - vinyl proton signals of hex-1-ene;

OLIG - vinyl proton signals of hex-1-ene oligomers;

INT - vinyl proton signals of hex-2-ene;

CH_2&CH - aliphatic methylene and methine proton signals.

The conversion of the monomer to give oligomers can be estimated from the relation:

$$Conv = (CH_2\&CH–2\times SUB–INT–1)/(CH_2\&CH–1)$$

The degree of oligomerization P_n can be found using the expression

$$P_n = 2\times(CH_2\&CH–2\times SUB–INT–1)/(9\times OLIG)$$

The number of hex-2-enes can be calculated as

$$INT/(CH2\&CH–1)$$

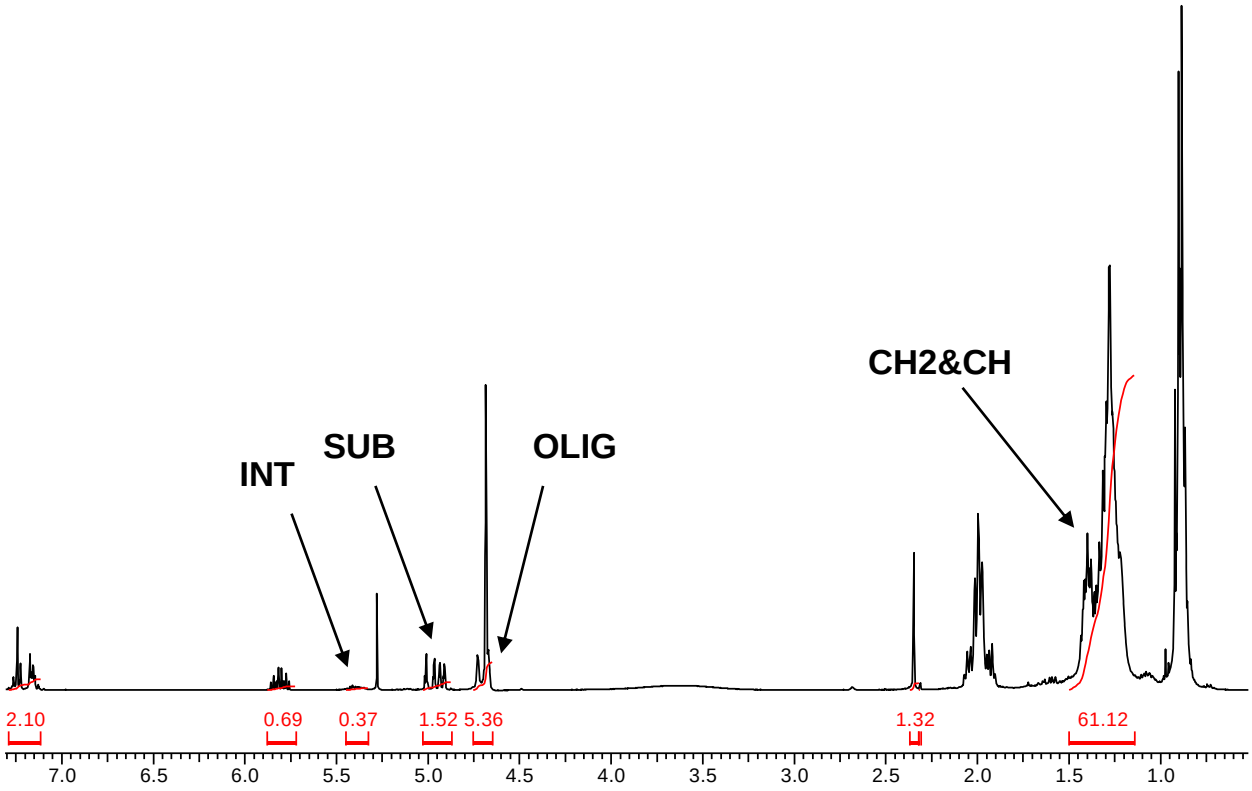

Figure S7 Integrated intensities to estimate the monomer conversion and oligomerization grade (zirconocene **4**).

This procedure has low accuracy and we used it here for approximate evaluation of the productivity of zirconocenes catalyzing the formation of higher oligomers.

S5. Crystal structure determination of 4

Crystals of **4** suitable for X-ray study were obtained by diffusion crystallization from toluene solution of the complex in the atmosphere of hexane. A single yellow crystal of **4** with

approximate dimensions 0.40 × 0.40 × 0.25 mm was mounted using an inert oil in the hole of plastic CryoLoop and transferred to a cold air stream on the Bruker SMART APEX II diffractometer.

Absorption correction based on measurements of equivalent reflections was applied. [1] The structure was solved by direct methods [2] and refined by full matrix least-squares on F^2 [3] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions and refined using a riding model.

References

1. G. M. Sheldrick, *SADABS, Program for scaling and correction of area detector data*, University of Göttingen, Germany, 1997.

2. G. M. Sheldrick, *Acta. Crystallogr*., 2008, **A64**, 112.

3. G. M. Sheldrick, *Acta. Crystallogr*., 2015, **C71**, 3.